

PHOSPHORUS CYCLING IN SOUTHEASTERN PIEDMONT LAKES: AN ALTERNATIVE PATHWAY

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Abstract. The phosphorus cycling paradigm in lakes is based on data from systems in northern temperate regions. Anoxic respiration in the hypolimnion of north-temperate lakes creates strongly reducing conditions that liberate dissolved inorganic phosphorus (DIP) from settling particulates. Hypolimnetic DIP steadily increases during summer stratification as phosphorus is liberated, and is mixed throughout the water column at fall overturn. This paradigm fails to explain phosphorus cycling in Southeastern Piedmont lakes. No increase in DIP is found in the anoxic hypolimnion during summer stratification; nor is an increase in DIP observed during fall overturn. We hypothesize that the conventional paradigm is not appropriate in iron-rich Southeastern Piedmont lakes because: a) iron-oxide sorption reduces the bioavailability of DIP, and b) the abundance of oxidized iron prevents DIP accumulation in the anoxic hypolimnion. We use iron-oxide chemistry to develop an alternate phosphorus cycling pathway: DIP is released from iron-phosphate particulates when pH increases due to photosynthesis. This mechanism forms a biogeochemical feedback loop that enhances algal blooms.

INTRODUCTION

The scientific basis for the conventional paradigm of phosphorus cycling in lakes was developed with data primarily from north-temperate systems (Hutchinson 1957, Rodhe 1969, Carlson 1977). This paradigm involves the sinking of inorganic particulates and organic material from the surface (epilimnetic) waters to the hypolimnetic waters of lakes during summer stratification. The depletion of oxygen and anoxic respiration in the hypolimnion creates reducing conditions in the buffered waters of north-temperate lakes. As iron-phosphorus compounds are reduced and organic matter is decomposed in the anoxic hypolimnion, there is a steady increase in DIP which is circulated to the lake at fall mixis. (Hutchinson 1957; Wetzel 1983; Goldman and Horne

1994). This phosphorus cycling paradigm fails to explain phosphorus cycling in Southeastern Piedmont lakes.

The climate in north-temperate regions provides for ice-covered lakes in winter that stratify thermally, with the colder water at the surface. These climatic conditions produce dimictic lake systems; lakes that stratify in both summer and winter and mix twice in the annual cycle, at fall overturn and at spring ice-out. In contrast, the climate in the Southeastern Piedmont provides for a longer growing season and warmer annual average temperatures than those found in north temperate regions. This difference in climate affects the length of time the lake is stratified, and the strength of disturbance needed to disrupt stratification. The lack of ice cover during the winter months is also important, creating monomictic rather than dimictic lake systems in the southeast US.

Climate is not the only difference between lakes in north-temperate regions and the Southeastern Piedmont. Differences in water chemistry and parent geology create conditions that prevent the accumulation of DIP in the anoxic hypolimnion and its subsequent circulation at fall mixis in lakes of the Southeastern Piedmont. We present the theoretical basis for a new pathway in the phosphorus cycle of Southeastern Piedmont lakes. Data to support hypotheses presented here are described elsewhere in Zeng and Rasmussen 2001, and Mayhew et al. 2001.

THE PHOSPHORUS CYCLE IN LAKES

Phosphorus (P) is considered the nutrient most frequently limiting to algal production in lakes (Hutchinson 1957; Rodhe 1967; Carlson 1977; Carpenter et al. 1998). Hence, elevated concentrations of P generally lead to an increase in nuisance algal blooms and lake eutrophication. Phosphorus occurs in lakes in both organic and inorganic forms. Total particulate P (comprised of bacterial, animal, and plant P, and suspended inorganic P) is generally present in much larger quantities than soluble P in most aquatic environments. Dissolved organic P (DOP) makes up the

bulk of total dissolved P. The small DIP fraction primarily occurs as orthophosphate (PO_4^{3-}). A fraction of total P is also found in colloidal form, but colloidal P does not usually comprise a significant fraction of total P (Goldman and Horne 1983).

The form of phosphorus most readily available for biological uptake is DIP. Bioavailability of DIP is restricted by its tendency to precipitate in the presence of bivalent metal (Ca^{2+} , Mg^{2+}) and ferric (Fe^{3+}) ions at neutral to alkaline pH, and its tendency to sorb to clay and other amorphous inorganic particles such as aluminum and iron oxides.

The ratio of precipitated to cycled phosphate is determined by water chemistry (such as high pH and cations which favor precipitation) and hydrological conditions (such as stratification) that may restrict the free movement of phosphate (Atlas and Bartha 1993). Turnover time for DIP in the epilimnion of stratified lakes as demonstrated by radio-tracer studies is rapid (minutes to hours), and is bacterially mediated (Rigler 1956; Hayes and Phillips 1958; Harrison et al. 1972). Most microbially-mediated phosphorus transformations can be viewed as transfers of inorganic to organic phosphate as DIP is incorporated into bacterial and algal biomass. However, transfers of insoluble, immobilized forms to soluble or mobile compounds and releases of DIP from the decomposition of organic matter are also microbially-mediated phosphorus transformations.

Phosphorus cycling in lake systems can be significantly affected by the iron cycle. Ferric oxides sorb DIP via ligand exchange. These ferric-phosphorus complexes can be transformed by reduction to the more soluble ferrous form, and by alkaline desorption at elevated pH; both transformations release sorbed phosphate. Biochemical transformations in a lake can only be understood in the context of redox potential and the related concentrations of iron (Hutchinson 1957).

THE IRON CYCLE IN LAKES

The cycling of iron consists primarily of oxidation-reduction reactions that reduce ferric to ferrous ions and oxidize ferrous to ferric ions. Amounts of iron in solution, and the rate of oxidation of ferrous to ferric iron in oxygenated water, primarily depends upon the pH, Eh, and temperature. Ferrous ions are oxidized spontaneously to the ferric form in alkaline to neutral conditions, and may be precipitated as ferric hydroxide in alkaline environments. These reactions are important in both inorganic and organic iron-containing compounds. Iron complexes

with certain organic molecules, by which the solubility and availability of iron is greatly altered. Elevated concentrations of complexed soluble iron are associated with high levels of humic acids, tannic acids, and other lignin derivatives which can act as chelating agents for ionic and charged colloidal iron.

Ferric hydroxide in oxygenated waters may be found as a flocculant (< 500 nm), or as a finely divided precipitate of ferric hydroxide that has the properties of a colloid (1 to 500 nm, charged). Colloidal particles of $\text{Fe}(\text{OH})_3$ commonly are positively charged, although a negative charge can occur at high pH. Ions in solution (including PO_4^{3-}) and negatively charged clay particles, organic colloids, and other suspended solids can neutralize the charges on the hydroxide colloidal particles. The uncharged aggregates join to form a rapidly settling precipitate. As pH increases (> 8), the colloidal particles may lose their positive charge and thus any complexed anions (Wetzel 1983). This release of anions is important in waters where algal photosynthesis elevates the local pH.

In environments of limited oxygen diffusion and significant heterotrophic microbial activity, anaerobic conditions may decrease the redox potential sufficiently (< 200 mV) to allow ferric iron to act as an electron sink and be reduced to Fe^{2+} , or precipitated as ferrous sulfide in the presence of H_2S (Hutchinson 1957; Atlas and Bartha 1993). Iron is more soluble in the ferrous state than in the ferric state, hence reduction of ferric-phosphate complexes solubilizes both iron and phosphorus. The reduction of ferric to ferrous forms is the mechanism that leads to elevated phosphate concentrations in the anoxic hypolimnion of lakes in the traditional phosphorus cycling paradigm.

Iron can be delivered to waterbodies as ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions, iron hydroxide ($\text{Fe}(\text{OH})_3$), iron oxyhydroxide (FeOOH), or complexed to calcium, phosphorus, and other anions (Figure 1). Once in a receiving waterbody, iron can be transformed via reduction, oxidation, and precipitation or biological consumption. The mobilization of insoluble ferric phosphates may occur when microorganisms reduce ferric ions to ferrous ions in the soil under anaerobic conditions. Flooding of soils enhances release of phosphate by this mechanism (Atlas and Bartha 1993).

The high iron content in the soils and resident parent material of the Georgia Piedmont results in significant transport of iron in runoff to receiving waterbodies. Hence, in the circum-neutral pH of the surface waters of the Georgia Piedmont, the availability of inorganic phosphate is likely controlled by the iron cycle.

AN ALTERNATE PHOSPHORUS CYCLING PATHWAY

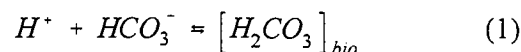
We propose a new pathway for phosphorus cycling in Southeastern Piedmont lakes. We hypothesize that the conventional phosphorus cycling paradigm is not appropriate in iron-rich Southeastern Piedmont lakes because: a) iron-oxide sorption reduces the bioavailability of DIP, and b) the abundance of oxidized iron prevents DIP accumulation in the anoxic hypolimnion. We use iron-oxide chemistry to develop an alternate phosphorus cycling pathway: DIP is released from iron-phosphate particulates by alkaline desorption when pH increases due to photosynthesis. This mechanism increases the DIP bioavailability and forms a bio-geochemical feedback loop that enhances algal blooms.

Iron is abundant in the Bt horizon soils of the Southeastern Piedmont. Sediment transport in runoff introduces abundant iron and phosphorus to receiving waterbodies, e.g., suspended solids concentration is highly correlated with total P concentration in Lake Lanier (Zeng and Rasmussen 2001). We postulate that the iron transported in runoff sorbs DIP and reduces its bioavailability in receiving waterbodies. An experimental test of the availability of phosphate measured as orthophosphate using the Murphy-Riley method of phosphate analysis is described in Mayhew et al. 2001. A small pond was fertilized on multiple occasions with different fertilizer treatments. The Bt horizon soil plus fertilizer treatment resulted in no significant increase of phosphate to the water column (see Mayhew et al. 2001, this volume). This study provides support for the hypothesis that iron sorption reduces the bioavailability of DIP.

The abundance of oxidized iron in the water column and sediments of Southeastern Piedmont lakes also prevents the accumulation of DIP in the anoxic hypolimnion. The lack of oxygen in the hypolimnion during summer stratification should lead to reducing conditions that would liberate DIP from iron-phosphate complexes. However, we have never measured iron in the ferrous form even in anoxic hypolimnia in the systems we have sampled; we have only measured iron in the ferric state (Rasmussen, unpublished data). Localized iron reduction may occur, but with abundant oxidized iron available any liberated phosphate is rapidly sorbed again. Depletion of oxygen and anoxic respiration are not sufficient to overcome the sorption capacity of oxidized iron in the hypolimnion, therefore soluble phosphorus does not accumulate in the hypolimnetic waters, nor circulate at fall mixis.

We present an alternate phosphorus cycling pathway appropriate for Southeastern Piedmont lakes in Figure 2. External DIP is delivered to the waterbody either in the presence or absence of sediment. In the conventional paradigm (indicated by the heavy solid line), settling organic and inorganic particulates are reduced in the conditions created by anoxic respiration in the hypolimnion during summer stratification. This reduction leads to an accumulation of soluble iron and DIP that becomes available for algal uptake at fall mixis.

Southeastern Piedmont lakes have iron-rich, low sulfate waters with little buffering capacity. This water chemistry creates a system that is very responsive to changes in pH. Algal photosynthesis during summer stratification can elevate local pH due to carbonate uptake:



The biological uptake of carbonate results in a concomitant increase in water pH in poorly buffered systems. Oxidized iron compounds release ions from ligand exchange at elevated pH (>8) (Stumm and Morgan 1996) in a process called alkaline desorption (Figure 1). Thus, the algae modify pH as they photosynthesize and create conditions that release DIP. Alkaline desorption can be expected to follow a diel cycle depending on the dominance of respiration or photosynthesis, and therefore pH, at a given time in the daily cycle. This mechanism of DIP release may serve to enhance and prolong algal blooms in systems with suspended iron-phosphate complexes.

In Southeastern Piedmont lakes (indicated by the heavy dashed line in Figure 2), ferric forms of iron are not reduced and soluble iron and phosphate are not released. Instead, oxidized iron transported in runoff sorbs DIP and reduces its bioavailability. Suspended iron oxide complexes lose their ligand exchange capacity at elevated pH (>8), and release DIP. Algal photosynthesis can elevate pH and thus forms a biogeochemical feedback

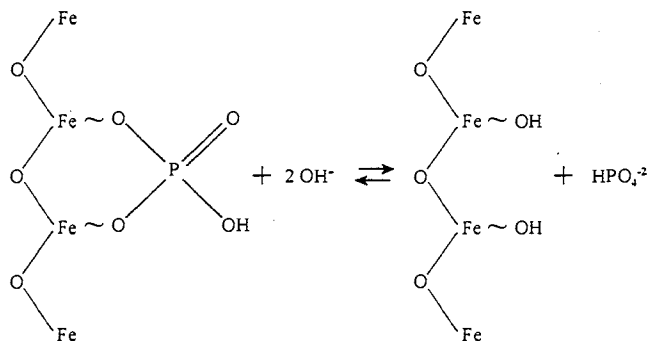


Figure 1. Iron-phosphorus reaction at elevated pH.
(See Stumm and Morgan 1996, p. 545.)

LITERATURE CITED

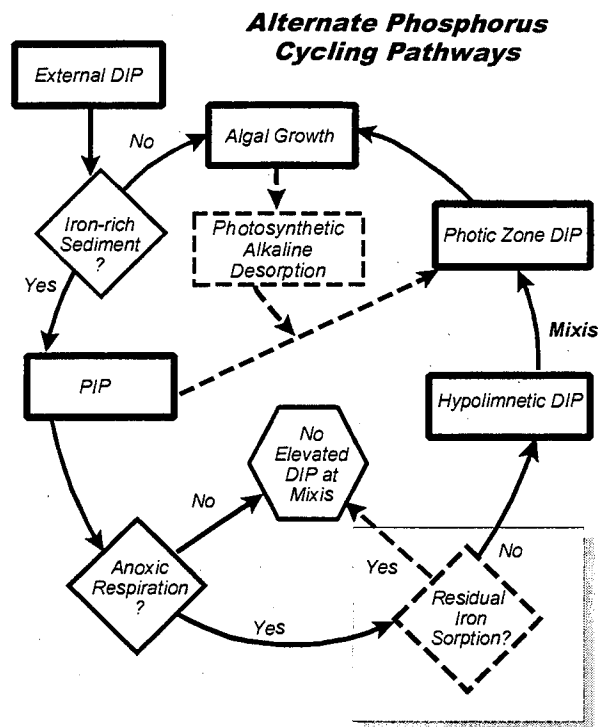


Figure 2. The conventional phosphorus cycling paradigm is indicated by the heavy solid lines. The alternative pathway is indicated by the heavy dashed lines.

loop via alkaline desorption.

FUTURE RESEARCH

We plan to conduct empirical tests of the hypotheses and phosphorus cycling pathway presented here. Empirical tests are designed to explore the iron-phosphorus relationship in three ways. First, the chemical relationships of iron and phosphorus are being defined in laboratory experiments. Second, interaction of organic matter on the phosphate sorption capacity of oxidized iron will also be tested in laboratory experiments. Finally, the ability of phytoplankton to cleave iron-sorbed phosphate will be tested in experimental cultures. The results of these experiments will further define the role of oxidized iron in the phosphorus cycling pathways of Southeastern Piedmont lakes.

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